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METHOD FOR THE WASHING AND/OR CLEANING OF SOILED TEXTILE GOODS

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The treatment of soiled textile goods in a washing bath, which contains surfactants and perhaps other components common in washing baths, using ultrasound effect. The washing bath also contains insoluble trapping agents for pigment and/or grease soils, which can be separated manually or mechanically from the cleaned goods. The trapping agents are polyquaternary ammonium compounds, preferably present, which are immobilized, on the surface of insoluble carrier materials. In a multistage procedure, soil that can be bleached and/or influenced enzymatically are removed following the removal of pigment and grease, using bleaching and/or enzymatically acting auxiliary [agents].

Claims

1. Method for the washing and/or cleaning of soiled textile goods by treatment in a surfactant-containing washing bath, if desired with the addition of other washing and/or cleaning auxiliaries, characterized by the fact that the loosening of pigment and/or grease soil is undertaken, at least in part, under the effect of ultrasound and the work is thereby carried out with a bath, which contains at least extensively insoluble trapping agents for the absorption of at least one part of the loosened pigment and/or grease soils, and these trapping agents can be removed, manually and/or mechanically, from the cleaned goods.

2. Method according to Claim 1, characterized by the fact that the work is carried out with undissolved trapping agents, present as solids, for pigment and/or grease soils, which prevent a substantial retransferring of the absorbed soil fractions under washing conditions.

3. Method according to Claims 1 and 2, characterized by the fact that within the framework of a combination treatment, the work is carried out with a joint use of enzymatically acting and/or bleaching, washing or cleansing aids, wherein preferably, the bleaching and/or the enzymatic cleaning is done, at least in part, following the ultrasound treatment for the removal of the pigment and/or grease soils.

4. Method according to Claims 1-3, characterized by the fact that the ultrasound treatment is carried out in the presence of very finely distributed solids, which are converted to a suspension in the washing bath.

5. Method according to Claims 1-4, characterized by the fact that the ultrasound treatment takes place on textile goods immersed in the bath; the textile goods are freed, at least to a large extent, of adhering, gaseous fractions, in particular air occlusions.

6. Method according to Claims 1-5, characterized by the fact that suspended, fine-particle solids are present in the immediate vicinity of the textile goods to be cleaned.

7. Method according to Claims 1-6, characterized by the fact that at least in part, trapping agents for the loosened pigment and/or grease soils, inert solids, and/or components of conventional textile detergents are used as undissolved, very fine-particle solids.

8. Method according to Claims 1-7, characterized by the fact that hard-to-dissolve surfactants and/or insoluble to hard-to-dissolve builder components of conventional detergent mixtures are used as very finely distributed solids at the method processing temperature of the ultrasound treatment.

9. Method according to Claims 1-8, characterized by the fact that with a multistage procedure, the enzymatic and/or bleaching work stages, following an initial ultrasound treatment, are also carried out with an application of ultrasound, preferably, however, in a chronological course, at least in part, without the application of ultrasound.

10. Method according to Claims 1-9, characterized by the fact that the subsequent work stages are carried out at least in the time period of the enzymatic action without substantial use of ultrasound.

11. Method according to Claims 1-10, characterized by the fact that in the subsequent work stages, intermittent, preferably short ultrasound treatment phases are provided, wherein in particular, a final acoustic irradiation stage can be provided, which appropriately is carried out in the presence of undissolved trapping agent fractions for soil particles.

12. Method according to Claims 1-11, characterized by the fact that the work is carried out with aqueous washing baths whose pH value can lie in the weakly acidic to the alkaline range, wherein the work can preferably be in the neutral range (approximately pH 6-8.5).

13. Method according to Claims 1-12, characterized by the fact that insoluble trapping agents for pigment and/or grease soils are used in flat form, for example, as a cloth, sheet, and/or film, as fibers or bundles of fibers, in particular, however, in the form of finely distributed solids which are preferably distributed, to a large extent, homogeneously in the washing bath.

14. Method according to Claims 1-13, characterized by the fact that insoluble finely divided soil trapping agents are used, which exhibit active surfaces of at least approximately 0.5 m^2/g, in particular, at least approximately 1 m^2/g.

15. Method according to Claims 1-14, characterized by the fact that soil trapping agents are used, which are of organic and/or inorganic--in particular, mineral--origin and have, immobilized, at least on their surface, a pigment- and or grease-soil-binding finish.

16. Method according to Claims 1-15, characterized by the fact that insoluble polycationic, oleophilic, and/or polyanionic soil trapping agents are used in the washing bath, which contain, immobilized, at least on their surface, an appropriate finish.

17. Method according to Claims 1-16, characterized by the fact that the surfactant and soil trapping agent in the washing bath are coordinated with one another in such a way that an immediate transfer of the loosened soil to the trapping agent surface can take place without any substantial retransferring to the textile goods to be cleaned.

18. Method according to Claims 1-17, characterized by the fact that the work is carried out with anionic surfactants and/or nonionic surfactants, together with an insoluble trapping agent containing polycationic elements, in particular for the loosening and binding of pigment soil in the washing bath.

19. Method according to Claims 1-18, characterized by the fact that the work is done with soil trapping agents, which have, at least on their surface, immobilized polyquaternary ammonium compounds (PQAV) or PQAV/surfactant complexes.

20. Method according to Claims 1-19, characterized by the fact that very fine-particle mineral solids, for example, insoluble metal oxides, carbonates, silicates, and/or aluminosilicates are used as insoluble trapping agents, on whose surface, PQAV or PQAV/surfactant complexes and/or polytertiary-amino compounds are borne in an immobilized manner.

21. Method according to Claims 1-20, characterized by the fact that the trapping agents used for the binding of dirt have the immobilized finishes on the surface in a thin layer, preferably with a layer of thickness no more than approximately 100 µm, in particular in the range of 1 µm and below.

22. Method according to Claims 1-21, characterized by the fact that at least in the stage of the loosening of the main fraction of pigment and/or grease soils, in addition to the insoluble trapping agents, the work is carried out with the joint use of additional fractions of finely divided solids in the washing bath, which preferably are rendered hydrophobic or have hydrophobic molecule fractions.

23. Method according to Claims 1-22, characterized by the fact that the work is carried out with washing baths which in part contain, undissolved, hydrophobic, finely divided mineral substances, for example, appropriately pretreated silicic acid and/or surfactants which are hard-to-dissolve at the processing temperature of the ultrasound treatment.

24. Method according to Claims 1-23, characterized by the fact that surfactant mixtures containing surfactants that are difficult to dissolve at the processing temperature of the ultrasonic treatment, are used in conjunction with readily soluble surfactants.

25. Method according to Claims 1-24, characterized by the fact that the ultrasonic treatment is carried out at temperatures up to approximately 80°C, preferably in an approximate range of room temperature 70°C.

26. Method according to Claims 1-25, characterized by the fact that the ultrasonic treatment is carried out with frequencies in the range of up to approximately 100 kHz, preferably in the range of approximately 20-60 kHz.

27. Method according to Claims 1-26, characterized by the fact that the work is carried out with mixed frequencies and/or sliding frequencies with continuous and/or pulsating acoustic irradiation.

28. Method according to Claims 1-27, characterized by the fact that with the acoustic irradiation, the work is carried out with power densities up to approximately 10 W/cm^2.

29. Method according to Claims 1-28, characterized by the fact that at least during the acoustic irradiation period, a gas phase, in particular air, is mixed with the washing bath, [and] in particular [the two] are becoming homogenized.

30. Method according to Claims 1-29, characterized by the fact that the work is done in several stages in such a way that the addition of enzymatic and/or bleaching auxiliaries to the washing bath is provided before and/or preferably, at least in part, also after the initial removal of pigment and/or fat soils.

31. Method according to Claims 1-30, characterized by the fact that the bleaching of dye soilings takes place, at least in part, using UV radiation.

32. Method according to Claims 1-31, characterized by the fact that in multistage work, the trapping agents loaded with pigment and/or grease soils are separated, at least in part, from the partially cleaned textile goods before the subsequent cleaning stages.

33. Method according to Claims 1-32, characterized by the fact that the textile goods are also moved, for example, rolled in the washing lye, in particular, directly during the acoustic irradiation stage, for the removal of the pigment and/or grease soils.

Description

The object of the invention is a new method for the washing and/or cleaning of soiled textile goods by treating in a surfactant-containing washing bath. The method in accordance with the invention is suitable for the improved removal of pigment and/or grease soilings, which can also be present with so-called problem soilings, for which removal, usually, washing and/or cleaning auxiliaries of a special type are required.

The best known examples of this are the joint usage of bleaching agents for, in particular, the oxidative bleaching of particularly resistant dye soilings and the joint usage of enzymatically active washing auxiliaries, in particular the known detergent proteases, for the removal, for example, of protein-based soilings, wherein the method of the invention can also make use of the joint usage of such additional cleansing aids.

The new method can be carried out in one or several stages, wherein the invention concerns in particular the improved multistage treatment of soiled textile goods, which, in addition to pigment and/or grease soilings, also have, at least in part, problem soilings, for example, of the aforementioned type.

The goal of instruction in accordance with the invention is the realization of, in fact, old wishful thinking, namely the facilitation of the washing or cleansing process of a textile by

the action of ultrasound on the washing bath, loaded with the soiled textile.

The cleaning of difficult[-to-clean] surfaces in aqueous and/or organic washing baths, with the effect of ultrasound, has been known for centuries and has been implemented on an industrial scale. The application of this technique to the washing or cleaning of textiles has also been known as wishful thinking for a long period of time. Up to now, however, no one has come up with any useful proposals for actual application. The probably most recent proposal provides for the treatment of the textile goods to be cleaned with ultrasound in clean water at room temperature, wherein the water is gassed with finely distributed air. Examination of this working method on textile samples with the standard soiling that is presently common, however, does not reveal any substantial cleaning effects, even when the ultrasound treatment is carried out for several hours.

The invention is based on the goal of now realizing a facilitated cleaning or washing with the effect of ultrasound for soiled textile goods. In particular, the goal of the invention is to determine the procedure that results for such an ultrasound-washing method, on the one hand, from the special characteristics of the textile goods and, on the other hand, from the manifold nature of possible soilings on textiles in everyday life, in connection with the effect of ultrasound on the washing bath.

Disclosed for the first time with the invention by means of the possible technical [advancement] of now extending ultrasound washing to the area of soiled textiles, the specified measures for the effective textile washing, including ultrasound treatment, are revealed. The instruction of the invention thus particularly concerns, on the one hand, the elements which are to be taken into

consideration in the stage of ultrasound washing. On the other hand, the instruction of the invention concerns the appropriate connection of such an ultrasound washing with, in fact, known, more extensive measures of textile washing or cleaning, in particular for the elimination of residual portions from the area of the so-called problem soilings.

Accordingly, the object of the invention is, in its most general form, a method for the washing and/or cleaning of soiled textile goods by treatment in a surfactant-containing washing bath, if desired with the addition of other washing and/or cleaning auxiliaries, wherein the new method is characterized by the fact that the loosening of pigment and/or grease soilings is undertaken, at least in part, with the action of ultrasound and the work is thereby done with a bath which contains, at least to a large extent, insoluble trapping agents for the absorption of at least one part of the loosened pigment and/or grease soils, wherein these trapping agents are designed in such a manner that they can be removed, manually and/or mechanically, from the cleaned material--and if desired, also from the washing bath--[and] can become worn out.

The undissolved trapping agents, used in the surfactant-containing washing bath in the method of the invention and present as solids, for the pigment and/or grease soils, loosened with the ultrasound action, are designed in such a way that under the washing conditions, they prevent a substantial retransferring of the absorbed soil portions to the textile goods to be cleaned. Details on this are explained below thoroughly.

In another specific embodiment, the invention concerns, in particular, measures that are appropriate within the framework of a combination treatment, in which the ultrasound washing is

preferably used to loosen pigment and/or grease soilings, whereas problem soilings which are not eliminated thereby or are not sufficiently eliminated, are treated in separate method steps of the washing method. In particular, in this specific embodiment of the method of the invention, a combination treatment is described, which works with the joint use of enzymatically acting and/or bleaching, washing or cleaning aids. In a particularly preferred specific embodiment, described in detail below, the bleaching and/or the enzymatic cleaning of the soiled textiles are, at least in part, carried out subsequent to a previous ultrasound treatment for the removal of at least the substantial part of the pigment and/or grease soiling. Such a previous ultrasound washing exposes the areas of the problem soilings for the separate and purposeful treatment of these soiling portions. It is clear that in an appropriate multistage method, a particularly effective and simplified elimination of residual problem soilings is possible. At the same time--but also by the other method conditions of the method of the invention--this facilitates the textile washing or cleaning with reduced chemical requirements and thus a substantial reduction in contamination of the water.

Finally, the invention concerns apparatuses that make it possible to conduct the method of the invention in accordance with the private area, in particular with household washing machines or in commercial use.

Ultrasound washing

From the numerous problems in using ultrasound washing on soiled textile goods, the most important parameters are first described below, which have a decisive influence on the washing

result, which are not described in the appropriate and comparable state of the art with regard to cleaning methods using ultrasound application on difficult[-to-clean] surfaces, and which do not appear there or are not given very serious consideration.

Investigations of the application on ultrasound washing on textiles have shown that the effects of ultrasound use, which this method facilitates and improves, are directed, in particular, to the removal of pigment or grease soilings. The loosening of these soil types from the textiles to be cleaned is promoted by the use of ultrasound, under suitable method conditions, in such a manner that often the almost complete loosening of these soiled portions, at temperatures that are at most moderately elevated, is possible within a period of a few minutes, perhaps even within a period of less than one minute. The removal of typical problem soilings, which in particular, require bleaching and/or an enzymatic effect, can also perhaps be favored by ultrasound, but such striking method improvements or reduced efforts as were observed for the removal of pigment and/or grease soilings do not, as a rule, appear. The method of the invention accordingly provides, in a preferred specific embodiment, the use of ultrasound as a washing aid, in particular in one method stage, which is directed at the elimination of pigment and/or grease soilings, wherein the following method stages can be provided, with or without ultrasound, in which the more stubborn residual soilings can be eliminated.

The facilitated loosening of pigment and/or grease soils with the technical methods in the treatment of difficult[-to-clean] surfaces with the action of ultrasound cannot be readily transferred to the area of textile washing. The reason for this concerns noncomparable starting conditions, of which--without a

claim to completeness--the following can be enumerated: the loading of a washing bath with textile goods which are layered over one another creates not only the shading problems which are, in fact, known for ultrasound textile washing; one has to take into consideration, in particular, the capacity and readiness of the textile material, which are, in fact, known, to reabsorb dispersed soil from the washing bath. These problems known from conventional textile washing appear with much greater intensity under the conditions of ultrasound washing in the washing bath which is filled with textiles and is usually not uniformly exposed to acoustic irradiation or ultrasound. The possible advantage of the facilitated soil loosening under the effect of sound is overcompensated by this disadvantage in such a way that already for this reason, the use of ultrasound washing has been out of the question up to now.

Other difficulties can arise from stubbornly retained air occlusions, which is a tendency of textiles based on or jointly using fibers of natural origin. One has to mention here, in particular, cotton, which both in the nonrefined as well as the so-called refined state--and here also with regard to the nowadays widespread mixed fabric--offers stubborn resistance to ultrasound cleaning, especially during the loosening of pigment and/or grease soilings. The previously unrecognized cause for these difficulties is probably, among other things, to be found in the fact that the progressing ultrasound wave breaks off at the liquid/gaseous interface, and accordingly, the penetration of the ultrasound wave into the frequently soiled interior region of the corresponding yarn structure is also shielded if this source of error is not eliminated by special measures, which are described within the framework of the invention. In comparison to the cleaning of the

difficult[-to-clean] surface, the following complicating condition is also true for textile washing: the powerful effects or shocks, which are, in fact, considerable, from the collapse of the cavities formed with the ultrasound effect due to cavitation, which, in any case, act only in the immediate vicinity, are apparently also captured by the elastic structure of the fibrous bundle in the textile goods in such a way that their transfer to the deeper regions of the multimesh fiber structure is inhibited. Therefore, starting conditions are already present [in the invention] for the process of soil loosening, which are very different from those of the known and industrially used cleaning of difficult[-to-clean] surfaces with the action of ultrasound.

For the method step of the cleaning with the action of ultrasound on textile materials, the invention provides, as an essential element, the joint use of so-called trapping agents for the absorption of at least one part of the loosened pigment and/or grease soils. These trapping agents are insoluble, as such, in the washing bath and are present in such a form that they can be separated, manually and/or mechanically, from the cleaned material, and if desired, from the washing bath used.

As those insoluble trapping substances, especially the corresponding components described in the older Patent Applications Nos. P 3,545,990.5 (D 7478/7495), P 3,605,716.9 (D 7538), and in particular in the older Patent Application No. P 3,606,729.6 (D 7554), can be taken into consideration.

A first class of such trapping substances, which is particularly important in accordance with the invention, refers to insoluble polyfunctional, quaternary ammonium compounds (PQAV) and/or PQAV which are present, immobilized, on corresponding insoluble solid carriers and which are used, in particular, in the

form of their insoluble or immobilized PQAV/surfactant complexes and are described in detail in the older applications and here, once again, in particular in Patent Application No. P 3,606,729.6 (D 7554). The disclosure of the aforementioned older applications and in particular, the latter application is herewith explicitly made also the object of the invention description under consideration.

The older Patent Application No. P 3,545,990.5 (D 7478/7495) describes the use of polyfunctional quaternary ammonium compounds (PQAV), which are, at least to a large extent, insoluble in aqueous washing or cleansing solutions and/or are present, immobilized, on solids which are correspondingly insoluble in these aqueous solutions, as soil-collecting, cleaning reinforcers in aqueous washing and cleaning solutions, which can be removed from the material to be cleaned, manually and/or mechanically, after the washing or cleaning. This older application describes, in particular, the washing power reinforcement of common aqueous-alkaline textile detergent solutions by the joint use of such PQAV soil collectors. At least a considerable portion of the soil solubilized during the washing of the textile, in particular pigment soil, is absorbed by the PQAV present in the solid phase and thus, in the end, transferred from the originally soiled textile material to be cleaned to the soil [sic] collector. In this way, an increase in the reflectance values of the washed material can be established in the washing result.

The teaching of the older Patent Application No. P 3,605,716.9 (D 7538) modifies the use of such PQAV, which are, at least to a large extent, insoluble in aqueous washing and cleaning solutions and/or are present, immobilized, on solids, which are correspondingly insoluble in these aqueous solutions, to the effect

that the new PQAV-containing auxiliaries are used for the regeneration of soil-laden cleaning baths, in particular for their subsequent reutilization. According to the teaching of this patent, in particular aqueous-alkaline, if desired surfactant-containing cleaning baths, [and] in particular washing solutions from the textile washing, can be subjected to regeneration in such a way that either already during the textile washing and/or subsequent to it, the soiled cleaning bath is treated with the insoluble or immobilized PQAV, and in this way, at least in part, is freed from the solubilized soil, in particular, pigment soil. In particular, activated PQAV compounds, which were already produced by a reaction of the PQAV with anion-surfactant components before the use of these trapping agents in, for example, anion-surfactant washing baths, are described here as particularly suitable trapping agents.

The use of corresponding PQAV or PQAV/surfactant complex compounds, from the reaction of PQAV with surfactant components, in particular, anionic, amphoteric, and/or nonionic surface active agents, as a dirt-absorbing reduction agent for the lowering of the chemical requirement of conventional washing and/or cleaning agents is the object of the aforementioned older Patent Application No. P 3,606,729.6 (D 7554). With the joint use of such trapping agents, which are insoluble in the washing bath, it is possible, for example, to do without the joint use of common phosphate-containing and/or phosphate-free builder components, [either] partially or entirely. Also, the quantity of surfactant components can be reduced in comparison to the usual quantity used. Furthermore, for example, it is possible to do without the joint use of common soil carriers, for example, of the type of the carboxymethylcellulose. It is also possible to do without the joint use of common washing alkalis, partially or entirely, since it has been shown that such

PQAV-based soil trapping agents can be used particularly effectively in the neutral to weak-alkaline range, preferably in the range of approximately 7 to 8.5. The last-mentioned application also explicitly describes the use of such chemically depleted detergent systems in washing baths with the action of ultrasound, in particular under the conditions of textile ultrasound washing. The following general data (to be understood as particularly exemplary) from the cited older applications regarding the PQAV to be used or the PQAV/surfactant complexes derived therefrom, are also valid for the teaching of the invention under consideration:

Polyfunctional quaternary ammonium compounds (PQAV) have been described and are known in the most varied forms in the documents of the state of the art and also on the market. An important field of application for such compounds is the area of cosmetic preparations, in particular for treating or conditioning hair. A known characteristic of the PQAV is that they can be absorbed on solid surfaces, wherein this capability is also available in particular in the presence of common surfactant components. Depending on the constitution, the absorption capacity and the adhesiveness of the PQAV on the solid substrate are present in various degrees. Individually, the specific constitution of the PQAV plays a decisive role [with this invention]. In general, these previously known PQAV are oligomers and/or polymers which have a plurality or a large number of quaternary ammonium groups on their oligomeric or polymeric matrix. For use in the area of cosmetics, a sufficient water solubility of the PQAV is generally required. The use of the PQAV in accordance with the invention, on the other hand, requires the insolubility, or at least sufficient insolubility, of the PQAV-based cleaning reinforcers, used as the

soil collectors, in the aqueous washing or cleaning solutions. However, in an important specific embodiment of the invention, all previously known water-soluble PQAV components can be supplied to the application purpose in accordance with the invention. To this end, namely, it is merely necessary to fix and thus to immobilize the, in fact, water-soluble and/or water-swelling PQAV components of the state of the art on sufficiently water-insoluble carriers so that they are not washed off or are not substantially washed off from this carrier during the cleaning process. As will be described in detail later, there are a large number of possibilities available for this. With this, however, it is already clear that for the purposes of the invention, all especially oligomeric and/or polymeric polyfunctional quaternary ammonium compounds known from the state of the art, which can be produced either in a completely synthetic manner or with the joint use of natural substances and their modification, can be used.

From the comprehensive, appropriate literature, one can cite as examples the following documents, whose disclosure is herewith also made explicitly the object of the disclosure of the invention description under consideration for the structure of the PQAV: U.S. Patents Nos. 3,589,978; 3,632,559; 3,910,862; 4,157,388; 4,240,450; and 4,292,212; British Patent No. 1,136,842; German Patent No. 2,727,255 (Auslegeschrift), as well as the U.S. Patent No. 3,4,72,840 mentioned therein.

Suitable water-soluble or water-insoluble PQAV in the sense of the invention preferably have an average molecular weight of at least and approximately 200, preferably at least and approximately 300, and in particular at least and approximately 1000. The upper limit of the PQAV is basically meaningless and, for example, is

50 million, for example, 10 million. This is understandable because of the condition of water insolubility required in accordance with the invention. This condition of a sufficient insolubility or immobilization determines, in the end, the lower limit of the average molecular weight also, so that the indicated numerical values acquire an exemplary character, taking into account this additional consideration.

After a suitable preparation, described below, all polymers which carry quaternary ammonium groups in the polymer chain or bound to the polymer chain are suitable for the purposes of the invention as initially water-soluble PQAV, but then PQAV immobilized on a water-soluble carrier. Such quaternary ammonium groups can be derived also from cyclically bound nitrogen. Examples of such quaternary ammonium groups are corresponding members of 5- or 6-membered ring systems, for example, of morpholine, piperidine, piperazine, or indazole rings. Numerous examples of such water-soluble PQAV are, for example, described in more detail in U.S. Patent No. 4,240,450.

Homopolymers or copolymers with cyclic units, as they are known individually from U.S. Patent No. 3,912,808, can be preferably suitable. Commercial products of this structure are, for example, Merquat® 100 and Marquart® 550 (Quaternium 41).

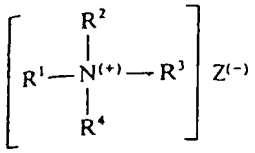
Other preferably suitable PQAV are, for example, cellulose ethers whose anhydroglucose units carry 1-3 ether oxygen-bound substituents with quaternary ammonium groups. A commercial product with this structure is, for example, polymer-JR® 400.

Other particularly suitable cationic polymers are, for example, the quaternary polyvinylpyrrolidone polymers which are known from U.S. Patent No. 3,910,862 and, which can be obtained, for example, under the tradename Gafquat® 734 and 755, and the

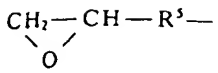
quaternary polymeric urea derivatives, which are known from U.S. Patent No. 4,157,388 and can be obtained, for example, under the tradename Mirapol® A 15.

Preferably suitable PQAV can be those compounds which in solid form cause problems during dissolution in water. Such cationic polymers are, above all, the cationic polygalactomannan derivatives known from British Patent No. 1,136,842.

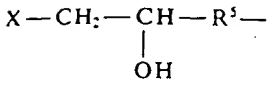
Galactomannans are polysaccharides which occur in the endosperm cells of many legume seeds, which, however, can be obtained on an industrial scale, only from locust bean gum, guar gum, and tara gum. They are synthesized from a linear mannan main chain, consisting of beta-(1,4)-glycosidically linked mannopyranose components, to which individual galactopyranose radicals in alpha-(1,6)-glycosidic bonding are fixed as a branch. The individual polygalactomannans differ mainly in the mannose-galactose ratio. The cationic derivatives of the polygalactomannans are produced by a reaction of hydroxyl groups of the polysaccharide with reactive quaternary ammonium compounds. Those of the following general formula, for example, are suitable as reactive quaternary ammonium compounds:



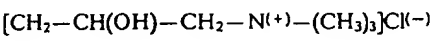
in which R^1, R^2, and R^3 are, for example, methyl or ethyl groups and R^4, an epoxyalkyl group of the following formula:



or a halohydrin group of the following formula:



in which R^5 is an alkylene group with 1-3 C atoms; X = chlorine or bromine; and Z, an anion, such as chloride, bromide, iodide, or hydrogen sulfate. The degree of substitution should be at least 0.01, and preferably at least 0.05, and frequently is between 0.05-1. A particularly suitable quaternary ammonium derivative of a polygalactomannan is, for example, the guar hydroxypropyl trimethylammonium chloride, which carries cationic groups of the following formula:



bound to the oxygen atoms of the hydroxyl groups of the polysaccharide. Such cationic guar derivatives are, for example, on the market under the tradename "Cosmedia Guar C 261." The degree of

substitution (DS) of Cosmedia Guar C 216 is, for example, approximately 0.5. Also the commercial products "Jaguar C-13" (DS = 0.11-0.13) and "Jaguar C 13 S" (DS = 0.13) belong to this type.

In particular, corresponding PQAV-surfactant complexes, which can be derived from the reaction of such PQAV components with one or more surfactants and in particular, anionic surfactants, amphoteric surfactants, and/or nonionic surfactants, are suitable as soil-trapping agents for the textile washing stage, described in accordance with the invention, using ultrasound. In this reaction, the originally present counteranion of the PQAV is, at least in part, possibly replaced by surface-active agents. It may thereby be preferable to use corresponding reaction products between the original PQAV and the surface-active agents, in which at least 50 Eq% and in particular, at least and approximately 80 Eq% of the quaternary ammonium groups, with regard to their counteranion, are activated by an exchange with the surface-active agents. In the preferred specific embodiment of the invention, the activation of the quaternary ammonium groups is undertaken by the use of at least equivalent quantities of PQAV, on the one hand, and surface-active agents, on the other hand, in the preliminary production stage of the soil-absorbing trapping agent. Excesses of the surface-active agents generally are not harmful and can even be preferred. Thus, particularly active trapping agents have been obtained by using a multiple excess of the surfactant components beyond the stoichiometrically needed quantity. This excess can, for example, make up to 10-fold of the stoichiometrically calculated amount or even more.

In particular, surfactant components capable of such an exchange are used as surface-active agents. In quaternary ammonium groups, as is known depending on the type of quaternization reaction, a halide or a lower alkyl sulfate group, for example, is usually present as a counteranion. In accordance with the invention, this counterion is, for example, replaced by surfactants containing anionic groups or correspondingly reacting surfactants. Thus, the counteranion can be replaced by, in fact, known anionic, amphoteric, and/or nonionic surface-active agents, in particular by corresponding low-molecular compounds with a surfactant character. In fact, it is known that PQAV components are accessible to such a reaction with, in particular, anionic surfactants and thereby form precipitation products with reduced solubility. The invention makes use of this known reaction, since it has been shown that particularly active soil absorbers are then present, if this reaction with the surfactant components has already taken place before the use of the soil-collecting absorbers in the washing or cleaning solution.

The reaction between PQAV in the original form and, for example, anionic surfactant-acting components already takes place at room temperature, but can be promoted and/or shortened by an elevation of the temperature. If, for example, quaternary ammonium group-containing polymer compounds in their original form, that is, with their original counteranion, are brought as an impregnating agent to a solid, for example, a cloth, and simultaneous with it or subsequent to it, an anionic surfactant component is applied additionally as an impregnating agent in at least equivalent quantities, then these two components already react during storage at room temperature to form the PQAV type of the desired high absorption activity. The formation of such PQAV/surfactant

complexes can be promoted and shortened in that the reaction of the surfactants with the PQAV, if desired with the joint use of solvents, is carried out at an elevated temperature. For example, temperatures above 60°C and in particular, temperatures above 95°C, are regarded as suitable. Thus, especially in the coating of mineral carriers, a short-term heating to temperatures in the range from approximately 100-230°C, preferably to temperatures in the range from approximately 100-150°C, may be suitable to ensure the desired highly active absorption state of the soil collectors. Within the scope of the invention, PQAV/surfactant complexes, which were formed in the presence of the insoluble solid phase, or better stated, in situ on the surface of the solid phase, may be preferred. In this way, it is possible to use PQAV soil absorbers, which contain, immobilized, a PQAV/surfactant complex-impregnating agent on the surface of an insoluble, organic or inorganic carrier, which was produced by the reaction of an originally soluble and/or capable-of-swelling (and thereby, particularly water-soluble) PQAV with the surface-active agents. In one operation, the immobilization of the PQAV here on the surface of the insoluble solids is connected with the desired activation of the PQAV impregnation to the particularly reactive state of soil absorption.

If the solubility of such PQAV/surfactant complexes has not yet declined sufficiently, so that one must expect a retransfer of these complexes to the material to be cleaned, the desired insoluble state of this impregnating mass can be attained by a crosslinking of the PQAV-containing impregnating mass, for example, by means of polyfunctional crosslinking components, in a manner which is, in fact, known.

The general regularities, as they are described in the aforementioned older patent applications and in particular in Patent Application No. P 3,606,729.6 (D 7554), in particular for the interaction between the surfactant-containing bath and the PQAV-based trapping agents present undissolved therein, are valid for the textile washing method in accordance with the invention and particularly for the facilitated and accelerated loosening of pigment and/or grease soilings, brought about by the use of ultrasound. The detergent system that overcomes the pigment or grease soil problems can be reduced to the suitable combination of the two following components: auxiliary agents for the loosening of the soil contamination from the material to be cleaned and soil-absorbing, insoluble or immobilized trapping agents in the sense of the invention. To overcome pigment soil problems, at least in part, insoluble or immobilized PQAV are jointly used, as a rule, in the trapping agent system in accordance with the invention.

The auxiliary agents for soil loosening and transfer of the loosened soil onto the undissolved trapping agents are surfactants. Their characteristics and quantity can no longer be regarded without taking into consideration that these surfactants used as washing auxiliary agents also have a decisive importance for the solubilization of the loosened pigment soil in the bath. In particular, the data of the aforementioned older Patent Application No. P 3,606,729 (D 7554) are valid here.

In a preferred specific embodiment of the method under consideration, it is also important to reduce the quantity of the surfactant component, in comparison to the surfactant quantities used in conventional washing and cleansing agents, wherein considerable savings are possible without incurring substantial losses in the washing result. Not only does the reduction of the

surfactant quantity play a role thereby, but also the type of surfactant to be selected is influenced by the new goal formulation of their importance in the new washing method. Thus, excellent washing results were obtained using only one surfactant class which, in fact, hardly has any significance in conventional detergent formulations, but rather is used in the area of cleansing personal hygiene agents. Here we are dealing with the class of ether sulfates, in particular fatty alcohol ether sulfates, which contain, for example, 1-5 ring-opening ethylene oxide radicals as the polymer segment. As a whole, it is possible, in accordance with the invention, to work exclusively or predominantly with the surfactant components selected in a certain way, which, for example, are characterized by special ecological safety and/or by particularly rapid degradability. As examples of these surfactants, one can mention the known fatty alcohol sulfates, fatty alcohol ether sulfates, disalts of alpha-sulfonic acids, alpha-sulfonic acid methyl ester salts, and/or alkylglycosides. The principle of the conclusions in accordance with the invention is, however, not limited to these specific surfactants.

Very generally, one can take into consideration surfactant classes which can be utilized in actual practice, which can be subsumed in particular under the terms of anionic surfactants, nonionic surfactants, and/or amphoteric surfactants. If one considers that effective cleaning requires not only the elimination of pigment soil, then it is understandable that precisely the application of surfactant mixtures can be useful. Basically, however, it is valid that the quantity of the total needed surfactants can be clearly reduced in comparison to conventional detergent formulations.

Furthermore, it is common knowledge of detergent formulation that the use of synthetic surface-active compounds, especially from the class of the aforementioned surfactants, usually requires the joint use of so-called builder systems. The common builder that is widely used, sodium tripolyphosphate, is now being replaced, totally or partially, by phosphate-free builder systems, wherein here in particular, the synthetic crystalline aluminosilicates of the sodium zeolite A type have special importance. Together with these main components of the builder systems, however, the joint use of soluble cobuilders is usually considered to be necessary. Known and widely used cobuilders are, in particular, soluble, perhaps however, also insoluble, components able to bind calcium in a complex manner or to precipitate it. The cobuilders should, in particular, also facilitate the loosening of the soil from the material to be cleaned by breaking it up and to facilitate the transport of the bound and/or precipitated metal ions, in particular alkaline-earth metal ions, for absorption by the main builder component.

In accordance with the conclusion of Patent Applicant No. P 3,606,729.6 (D 7554), it has been shown that surfactant-containing formulations which contain trapping agents in accordance with the invention, in particular on the basis of insoluble and/or immobilized PQAV, can, totally or at least partially, do without the joint use of common phosphate-containing and/or phosphate-free builder components, without having to accept substantial limitations of the washing result. If the surfactant components are selected in such a way that they can sufficiently comply with their task of loosening the soil, then the insoluble or immobilized trapping agents take over the additional task of eliminating the loosened particle soil during complex washing. A retransfer of the

soil onto the material to be cleaned does not take place, so that high reflectance values can be attained even with a complete absence of common builder components.

The suspension of solubilized soil particles is usually supported in conventional detergent formulations by jointly using so-called soil carriers such as carboxymethylcellulose or corresponding polymeric soluble components. In accordance with the invention, it is possible to do without the joint use of these conventional soil carriers, totally or partially. Interestingly, it has been shown that in preferred specific embodiments of the invention, however, other components which were previously regarded as indispensable are also no longer needed. Here we are dealing in particular with the class of washing alkalis.

Conventional detergents and cleansing agents work with relatively strong alkaline pH values, wherein the corresponding pH range is ensured by the joint use of these soluble washing alkalis. Typical washing alkalis are, for example, water glass, soda, and the like. In the washing method in accordance with the invention, the establishment of correspondingly strong alkaline pH values is not required. The work can be carried out in a neutral to weakly alkaline range. To this end, buffer systems which, for example, hold the pH of washing and/or cleaning bath in the neutral range to at most a weakly alkaline range can be used in a manner which is, in fact, known. Numerically, this means that for example, the washing can be carried out in the range of approximately 6-9, in particular of approximately 7-8.5.

As described in particular in the older applications, the PQAV-based, insoluble trapping agents can be used in the form of a sheet or film or also in the form of a jointly used cloth. In particular, however, it is preferred, in accordance with the

invention, to use these essential auxiliary agents in the form of finely distributed solids which make possible their dispersed, fine distribution in the washing or cleaning baths, and thus ensure that with the most homogeneous distribution of the soil-adsorbing PQAV possible [is reached], each soiled area of the material to be cleaned is rinsed by the adsorption-ready PQAV. The transport path of the loosened soil particle from its original place to the desired deposition place on the trapping agent surface is kept as short as possible in this way. By the movement and thorough mixing of the material to be cleaned, which are also preferably used under the conditions of the ultrasound action in accordance with the invention, new adsorption-ready PQAV areas of the surface of the material from which the pigment soil is to be unloaded are also constantly made available in this way. This makes the limitation of the still- required surfactant performance and the considerations derived therefrom for the selection and/or reduction of the surfactants or surfactant quantity understandable.

The PQAV-based trapping agents present as a heterogeneous solid phase, in accordance with the invention, absorb, in particular, negatively charged fractions, for example, corresponding soil particles from the soil-laden bath. In addition, as a result of other surface forces, the PQAV solid material can have a cleaning or cleaning-reinforcing effect. In other important specific embodiments described below, it is consciously assumed that not only negatively charged soil fractions are to be removed in solid washing baths.

With conventional washing methods, greasy or oil, soilings present, for example, are hydrophilized to the extent that they are dissolved in the washing liquor. In an important specific embodiment of the invention, an auxiliary characterized by a high

absorption capacity for oleophilic soilings is also used in the heterogeneous solid phase, together with the soil-collecting PQAV. It is known that selected plastics, for example, polyethylene or polypropylene or polyurethane or also insoluble solids of arbitrary origin, with a strong, superficial hydrophobic finish, have the capacity of attracting to themselves the oleophilic soiled fraction, which was hydrophilized with the action of surfactants from a washing bath, and to retain it on their surface. This working principle is also used in this specific embodiment for the effective cleaning of soiled washing baths. The collectors for such oleophilic soil can, for example, be used in the form of flakes, fibers, or fibrous structures, such as cloths, randomly laid nonwoven fabrics, poromeric fleeces, and the like. Merely the condition indicated before for the PQAV cleaning agents, that a manual and/or mechanical separation between the liquid phase and the soiled collector present in the solid phase be ensured, is essential for this component. A particularly important specific embodiment will also be discussed in the following.

The use of the oleophilic, soil-collecting auxiliary agents can take place simultaneously with the treatment in the washing bath by PQAV and/or separately therefrom. The individual working conditions are determined by the nature of the soiling in the washing bath and the thereby-expected contamination of the soil-collecting auxiliary agents in the solid phase. In another important specific embodiment of the invention, polyanionic cleaning auxiliary agents also present in a separate solid phase are jointly used, in addition to the PQAV-based trapping agents and the oleophilic soil-collecting solids. Polyanionic components in dissolved and/or undissolved form play a considerable role in detergents and cleansing agents, which are common at present. They

are, for example, used as builders or cobuilders for the surfactants. They have a number of diverse tasks, wherein, as an example, the binding of calcium and/or magnesium ions from the prevailing water hardness can be mentioned. The specific embodiment of the invention affected here goes beyond this state of the art.

By means of the joint use of insoluble polyanionic components provided for in accordance with the invention, which, just as the previously discussed soil-collecting auxiliary agents are jointly used in a form which can be separated manually and/or mechanically, the removal of such soil or contamination fractions from the washing bath, which are positively charged, is possible. Such components can, for example, be formed during dye transfer or as decomposition products from bleaching processes. It is important in the conclusion of the invention that an undesired influence of the jointly used PQAV-based auxiliary agents and the polyanionic auxiliary agents discussed here cannot take place. Both collectors are provided as solid phases, spatially separated from one another in such a way that each of these auxiliary agents can develop its cleaning effect, without being impaired by the other undissolved auxiliary agents.

The conclusion in accordance with the invention comprises the joint use of the PQAV auxiliary agents and the polyanionic, insoluble auxiliary agents in the presence or also in the absence of the previously discussed third collector component, which is particularly suitable for the absorption of the oleophilic soils from the washing solution.

In particular, natural and/or synthetic solids with a majority of anionic acid radicals are suitable as an insoluble, polyanionic solid phase. As examples, one can mention insoluble components with a content of carboxyl groups, sulfonate radicals, phosphonate

groups and the like. It is known that it is precisely components of this type to which a strong washing power reinforcement is ascribed in the primary washing process. The use of this type as water-soluble components in textile detergents is widespread today; however, there are certain reservations against their use. In the specific embodiment discussed here, the conclusion of the invention provides for the joint use of such components in a heterogeneous solid phase and at the same time, in such a form that a separation of these solids with functional groups from the washing solution is possible so that the uncontrolled release of corresponding compounds into the wastewater is ruled out from the very beginning.

The insoluble, PQAV-based trapping agents used in accordance with the invention as soil-absorbing depletion agents are preferably used as a fine-particle solid, which is dispersed in the washing bath during the washing process, removed from the washed material after conclusion of the washing process, and if desired, finally, also can be separated from the cleaned washing liquor, as is described in detail in the aforementioned older Patent Application No. P 3,605,716.9 (D 7538). Any insoluble materials of an inorganic and/or organic type are suitable as insoluble carrier materials for the fixing of PQAV or PQAV/surfactant complexes and thus for the immobilization of these soil-collecting active components, provided that they, moreover, behave inertly in the washing solutions. Suitable organic materials can be, for example, of plant origin. However, inorganic carriers, as they are described in detail in the aforementioned older applications, are preferred. We are dealing here with mineral substances of a natural and/or synthetic origin, which are present in the form of finely divided solids. In accordance with the invention, PQAV-coated carrier substances of a specific surface of at least and approximately

0.5 m^2/g are preferably used, wherein, in particular, this specific surface is preferably at least 1 m^2/g. "Specific surface" is thereby understood to mean the flat area which can be coated with PQAV. Certain mineral substances which are particularly suitable here have, moreover, extensive surface areas in the interior of the solid phase, either because of their pore structure or because of their swelling capacity, which, however, are not accessible to a coating with PQAV or provide only limited access. The coatable external area can, however, attain considerable values, which can extend to or exceed 10 m^2/g and even 50 $m^2/2$ and leads to the area of 100 m^2/g or even beyond to, for example, 300 m^2/g. As examples of such extreme surfaces accessible to a coating with PQAV, one can mention colloidal silicic acids.

The maximum particle sizes of the PQAV-laden, very fine particles preferably do not have values above approximately 100 μm, preferably not above approximately 40 μm; these numerical values are based on the absolute particle diameters and signify that all or at least the preponderant majority of the fine particles present correspond to these framework conditions. Particles which exhibit an average particle size (volume average) of at most and approximately 10 μ, wherein the absolute size of at least the predominant fraction of all solid particles also lies below this value, are particularly appropriate for textile washing.

Suitable inorganic carriers are, in particular, insoluble and fine-particle salts, oxides, silicates and the like. Particularly suitable are, for example, aluminosilicates of the zeolite or zeolite-type compounds, in particular sodium zeolite A, which is widely used in detergents today. Zeolite A, and also in its exchanged form, for example, as a calcium salt, can be used in its place.

A particularly suitable mineral carrier class refers to swelling-capable, finely divided substances of the type of clays and/or the swelling-capable laminated silicates, in particular from the class of smectites. Swelling-capable inorganic minerals of this type are characterized by a particularly large surface in the swollen state. Use can be made of this within the framework of the invention. The known smectite clays, montmorillonite, hectorite, and/or saponite, are particularly suitable here. Suitable also, however, are comparable synthetic materials of only limited swelling capacity, as they are described, for example, in the older Patent Application No. P 3,526,405.5 (D 7031).

If the work is carried out with trapping agents which contain the insoluble active components, that is, for example, the PQAV/surfactant complex and/or the strongly oleophilic layer, as a surface finish of, in fact, inert, insoluble solids, then it may be preferable, in accordance with the invention, to provide these active surface finishes in as thin as possible a layer on the insoluble solid carriers. In this way, an optical utilization of the soil-collecting active masses is ensured. In this connection, it may be preferable, for example, to work with layer thicknesses of PQAV or PQAV/surfactant complexes on insoluble carriers, which do not exceed the range of approximately 100 µm or do so insubstantially. In a preferred specific embodiment of the invention, however, far smaller layer thicknesses of such PQAV collectors present in immobilized form are provided. If the work is carried out with finely distributed, coated carriers, for example, on a mineral basis, with a high specific surface, then the thickness of the PQAV-containing layer can extend here to the range of monomolecular layers, which, as is known, lies in the nanometer range (10^{-9} m). Preferably, layer thicknesses of the active

substance can accordingly find use on the carrier materials in the range up to approximately 1 µm and in particular, in average layer thicknesses up to approximately 10^{-1} µm or even only up to approximately 10^{-2} µm.

In particular here, the invention creates new, previously unknown possibilities for effective washing or cleaning. Even if one presupposes that on the basis of prior knowledge for the cleaning of solid surfaces, with the application of ultrasound, the facilitated loosening of pigment and or grease soils was basically known, nevertheless it could not be expected that under the same conditions of ultrasound action, it was possible to anchor loosened pigment soil and/or grease soil particles, conditioned by the joint use of surfactants, so securely on the surface of the trapping substrates used in accordance with the invention that the textile cleaning takes place without any substantial retransfer of the loosened soil fractions onto the textile material to be cleaned. Soil contamination of the bath can be managed without a lessening of the washing result, as is unknown in conventional textile washing. High degrees of whiteness or high reflectance values of the washed textile material are obtained under the conditions in accordance with the invention even when the washing bath is already very dark because of the intake of large soil quantities, provided that the absorption capacity of the trapping surfaces has not yet been exhausted. In the application of the previously described [patient], in which extremely thin layers of the trapping materials are on inert solid carriers, there is another important viewpoint for the surprising cost-efficiency and superiority of the new method in comparison to the prior art when these facts are considered.

The quantity of PQAV or PQAV/surfactant complex to be used in the detergent is coordinated with the expected soil load. If it is intended to use these soil absorbers only one time, then even the smallest quantities of these absorbers are sufficient, so as to bind the pigment soil usually yielded, for example, in the textile wash. PQAV components of the type affected here are able to bind the equivalent to several times their weight in pigment soil; this is particularly influenced by the spreading of the PQAV-based trapping agents on the carrier substrate in a very thin layer.

If, within the framework of the invention, soil-absorbing trapping agents containing an impregnating agent with PQAV or PQAV/surfactant complex on an organic and/or inorganic, insoluble carrier are used, then it may be preferable to keep the quantity of this impregnating agent, based on the total weight of the impregnated solid, in the range of approximately 0.01-20 wt% and in particular, in the range of approximately 0.1-10 wt%.

The textile cleaning stage with ultrasound application provided in the process according to the invention, in particular for the elimination of pigment and/or grease soilings, takes place in the preferred configuration in such a way that the material to be cleaned is, at least in part, preferably completely, immersed in the bath subjected to ultrasound, wherein it may be important to undertake measures so that the immersed material is freed, to a large extent, of adhering, gaseous fractions, in particular air occlusions. The cause of this is the already-described breakup of the sonic transfer at the liquid/gaseous interface, which can be reflected in the washing result to the effect that air occlusions retained in the fiber structure retain residual quantities of the soil load.

The careful, thorough soaking of the material to be cleaned with the liquid phase, before or at least during the ultrasound treatment, is appropriate in this connection. The joint use of so-called deaerator systems, as they are, in fact, known in textile technology, may be appropriate to facilitate this careful, thorough soaking and elimination of very fine air occlusions. As a rule, we are dealing here with selected components, in particular, surfactant components, which ensure the rapid penetration of the aqueous liquid phase to the interior regions themselves of such fibers or fiber bundles, which are otherwise accessible to the penetrating soaking only with difficulty. Such deaerator systems frequently contain, as is known, short-chain surfactants (components with a surfactant character based on hydrocarbon chains smaller than C_{12}). Mixtures of anionic and/or nonionic surfactants may thereby be used, for example, mixtures of several short-chain surfactants of the indicated type. Also, the solubility of the surfactants or surfactant combinations used in this connection is of significance for the deaeration effect. Thus, the joint use of a comparatively longer-chain, readily soluble surfactant with a comparatively short-chain, poorly soluble surfactant can lead to particularly fast deaeration effects. An example of this is the joint use of a C_{15} alkanesulfonate with a decyl alcohol, modified with approximately 2.9 ethylene oxide units. The prior art knows appropriate commercial products, whose joint use in the washing or cleaning baths used in accordance with the invention or in a prior soaking treatment of the textile material to be subjected to ultrasound washing is part of the invention.

In the process according to the invention with the use of ultrasound, it may be advantageous to additionally stimulate the tendency of the washing bath toward cavitation formation and

ultrasound action in that a sufficient quantity of fine-particle solids can, to a certain extent, be effective as cavitation nuclei. In the process in accordance with the invention, this will implement the cleaning-promoting principle already in the joint use of very fine-particle, insoluble trapping substrates, preferably homogeneously distributed in the washing bath. It is of particular importance thereby that these very fine-particle solids are present directly in the immediate vicinity of the textile material to be cleaned also and thus can be effective in promoting cavitation in the immediate vicinity of the soiling.

In addition to or instead of such trapping agents in very finely distributed solid form, it is also possible, however, in accordance with the invention, to jointly use other solids also in the washing bath, in particular to promote triggering of the cavitation. Here we may be dealing with selected active components of the detergent system or also solids foreign to the system, which are used only for the purpose of a reinforced cavitation formation.

At the process temperature of the ultrasound treatment, at least partially insoluble or poorly soluble, finely distributed components can be corresponding surfactants and/or insoluble to poorly soluble builder components of conventional detergent mixtures. Suitable surfactants are, for example, the poorly soluble disalts of alpha-sulfonic acids, which are hard to dissolve at lower temperatures of the washing bath, in particular of the C-number range of C_{12} to C_{18}, corresponding salts of alpha-sulfonic acids, in particular the corresponding methyl ester, but also other poorly soluble surfactant components, such as higher fatty alcohol sulfates and the like. In a configuration of the invention, mixtures of such poorly soluble surfactants are used with readily soluble surfactants. As a whole, the invention utilizes the fact

here that for the conditioning of the loosened pigment and/or greasy soil, only the smallest surfactant quantities are needed; after transfer of the loosened soil fractions to the trapping agents, they are again available for further soil loosening and conditioning. The undissolved surfactant fractions are used simultaneously as a surfactant reserve and for promotion and triggering of the cavitation in the immediate vicinity of the textile to be cleaned.

Conventional insoluble builder components, which can be used jointly for the same purpose, are, for example, very fine-particle, insoluble aluminosilicates of the type of detergent zeolites, in particular zeolite A and other mineral substances, as they have already been described here in connection with the description of the carriers for the PQAV trapping agents.

Very fine-particle, inert substances to promote cavitation formation are, for example, mineral substances such as insoluble silicic acid gels, as they are known, for example, as the commercial product "Aerosil." It may be appropriate to use these cavitation-promoting solids in hydrophobicized form or in a form which has at least hydrophobicized partial areas. The quantity of the jointly used, insoluble solids varies within broad limits and is, provided a sufficient effect is triggered, determined by appropriate considerations in the individual case. Thus, for example, up to 50 g/L washing bath, preferably up to 10 g/L washing bath may be appropriate, wherein in general, strong effects are already obtained up to 1-2 g/L.

The temperature of the washing bath during the ultrasound treatment can be up to approximately 95°C, but preferably is considerably below that and usually does not exceed temperatures of approximately 80°C. An effective cleaning is possible at room

temperature. The lowering of the process temperature towards room temperature is even preferred from the perspective of the promotion of a desired cavitation formation. On the other hand, one has to take into consideration that in the process according to the invention, a certain interplay of conventional effects of the textile cleaning by means of surfactants and the, in fact, known action of ultrasound cleaning is present. It has frequently proved appropriate to carry out the washing stage of ultrasound treatment in the temperature range of approximately 30 to approximately 70°C and here in particular in the temperature range of approximately 35 to approximately 50°C.

For the carrying out of the process in accordance with the invention in the stage of ultrasound treatment affected here, the entire frequency range known today and also, to some extent, used in cleaning methods can be taken into consideration as the frequency range. Particularly preferred acoustic irradiation frequencies lie in the range of up to approximately 100 kHz, wherein usually the lower limit for ultrasound is indicated as approximately 16 kHz. Accordingly, for example, a range of approximately 20-60 kHZ can be particularly suited for the sound frequency used, wherein it is also known, in turn, that the tendency toward cavitation formation and thus for the triggering of the desired cleaning power will be all the greater here, the lower the acoustic irradiation frequency in the range mentioned here is selected. However, the effects of far higher frequencies, for example, up to the MHz range, which are particularly characterized by a stronger material penetration capacity or power, are also known, even if, in fact, the tendency toward the promotion of cavitation formation declines here.

It has proved appropriate to move, in particular to roll, to compress, and/or to stretch the textile material to be cleaned, continuously and/or discontinuously, during the acoustic irradiation stage in the washing bath. In this way, not only are disadvantages of any possible areas compensated for, but also the removal of pigment soil, in particular, can be clearly accelerated.

The designing of the acoustic irradiation stage in the process of the invention or of the apparatuses suitable for the execution of this process stage is generally influenced by a number of parameters. As examples one can mention the following: composition and selection of the detergent system, size and degree of contamination of the cleaning bath, operating conditions of the cleaning bath, accessibility, service life, and energy consumption of the acoustic irradiation elements and expected degree of contamination of the apparatus in use, for example, in the sense of a practically continuous use in the field of commercial cleaning or merely periodic use in the area of personal household washing.

In the end, such considerations jointly determine that in the construction of the cleaning apparatuses, the stage of cleaning with ultrasound be conducted with a uniform frequency or with mixed frequencies, and/or with sliding frequencies with a continuous or pulsating acoustic irradiation. As a power density, values up to approximately 10 W/cm^2 and in particular, values in the range of approximately 0.5-5 W/cm^2 have proved especially useful and effective for the area of textile cleaning also, wherein the power input into a bath can be, for example, in the range of at least and approximately 20 W to a few hundred W. For larger baths, higher amounts are also suitable.

In a special configuration, the process in accordance with the invention makes use of a measure which has recently been proposed

for textile washing with ultrasound. Here we are dealing with the batchwise or preferably continuous dispersion of atmospheric oxygen in the aqueous washing bath. With upright washing apparatuses, the introduction and dispersion of the air can take place, in particular, in the lower area of the cleaning vessel, so that the washed material, perhaps with the joint use of introduced carrier elements, essentially comes into contact with a washing liquor that is saturated, or almost saturated, in dissolved air. If in this way, perhaps certain additional effects are also triggered, then this measure is not required, however, for the effective carrying out of ultrasonic washing in accordance with the invention.

Satisfactory washing results in the ultrasound stage are frequently obtained in the time period of 0.5-60 min, in particular, in 0.5-15 min, wherein a time period of approximately 1-15 min, in particular approximately 1-10 min, generally produces the desired cleaning effect.

The other stages of the cleaning process in accordance with the invention

In the preferred configuration, the invention provides a multistage cleaning process, which, in addition to the ultrasound treatment with the removal of pigment and/or grease soils, provides treatment of the textile material to be cleaned for the elimination of problem soils which still remain. It is thereby preferable to carry out these additional work stages, at least in part, following the ultrasound treatment. The advantage of this work is obvious. The problem soils now are present, freed of pigment and grease soils, and thus are accessible to the direct and purposeful attack of the individually used cleaning auxiliary agent.

The two most important additional cleaning auxiliary agents are dye-destroying, in particular bleaching additives, and enzymatically effective washing auxiliary agents, in particular detergent proteases.

With such a multistage procedure, the enzymatic and/or bleaching work stages following an initial ultrasound treatment also take place with the application of ultrasound; preferably, however, they are carried out in a chronological course, at least in part, without the application of ultrasound. That is in particular valid for a subsequent work stage with enzymatic action. Enzymes can, as is known, be sensitive with respect to the action of ultrasound to the point of ineffectiveness.

These considerations are less significant for the use of bleaching agents for the elimination of resistant dye soils. It has become evident, however, that bleaching is generally not so substantially promoted by the use of ultrasound so that the additional energy expenditure for this work stage pays off. It may be more sensible to provide, very simply, work stages in which the partially cleaned textile goods are now subjected to the bleaching and/or enzymatic treatment, perhaps with the setting of optimal working temperatures for these process steps, following the removal of pigment and/or grease soils. The textile goods to be treated in the bath are moved, if desired, batchwise or continuously, although not even this additional measure is required. Generally, the known conventional cleaning process is valid here.

The bleaching and/or enzymatic treatment can be carried out in the original bath containing the loaded soil trapping agents. In a special configuration of the invention, however, provision is made for the bath to carry out this process stage to be freed, at least

in part, from soil-laden trapping agents. This can take place, in particular, in such a way as described within the framework of the aforementioned older applications. Therefore, the bath can be pumped, for example, via separation stages, in which the soil-laden, undissolved trapping agent is retained.

The addition of the bleaching and/or enzymatically acting washing auxiliary agents to the bath can already have taken place from the very beginning and/or separately, following the ultrasound treatment stage. In particular, ultrasound-sensitive washing auxiliary agents are preferably added to the cleaning bath, following the first acoustic irradiation stage.

The measure to use auxiliary agents which are, in fact, unconventional as bleaching agents, described in the older applications and in particular, in Patent Application No. P 3,606,729.6 (D 7554), is of importance for the pertinent selection of the suitable process measure; in accordance with prior ideas, this measure has not been taken into consideration in actual practice because of the strongly alkaline textile washing baths. Examples for this are percarboxylic acid salts, which can be highly effective bleaching agents in the work stages following acoustic irradiation, in the pH range of approximately 6-8.5, which is useful in accordance with the invention.

In connection with these subsequent work stages, an intermittent, preferably short ultrasound treatment can be provided. Here, there is, in particular, the possibility of a corresponding, final acoustic irradiation stage, which is appropriately carried out in the presence of undissolved trapping agent fractions still with a free capacity for soil particles. In this way, one can ensure that, in such a final acoustic irradiation

phase, the last fractions of conditioned soil particles are also removed from the textile and from the washing bath.

An important work agent, which is in fact known and which can be used within the framework of the process of the invention, but now in a substantially more effective manner than before, is the bleaching treatment of stubborn dye soils by using UV irradiation. If such a work stage is placed, for example, at the end of the multistage washing process and the clarification of the washing bath from the soil-laden trapping particles is provided in particular for this as well, then use can be made of such a UV irradiation here in an effective bleaching action which was previously not known. As a whole, such a measure is used again for the goal of lowering the need for chemicals, and as a whole, is thus used to reduce environmental contamination by the washing bath which, in the end, is released into the wastewater system.

Other aspects of the invention

Finally, in another configuration, the invention concerns the apparatuses suitable for the carrying out of the process in accordance with the invention. This configuration comprises the entire area of textile washing, from individual household washing machines to commercial utilization of the new principle.

These apparatuses are characterized, in particular, by a container equipped with ultrasound-producing vibration elements, which represents the washing bath into which the washing liquor and the textile goods to be cleaned are introduced. Apparatuses to move the textile goods are preferably provided in the interior of this container, for example, to roll, compress, and/or stretch. The container is provided with an opening for the introduction and

removal of textile goods, which can preferably be closed, and has inlet openings that can be closed and exit openings that can be closed for the addition and removal of washing liquor. Also, metering devices for the optionally time-controlled addition of washing auxiliary agents in the sense of the process according to the invention are preferably provided, so that the preparation of the washing liquor, as a whole, is possible in the container equipped with vibrating elements, with the inflow of the liquid phase, in particular, tap water, in the non-softened or softened state.

One or more metering devices for detergent auxiliary agents can be controlled in the preferred configuration, automatically and time-staggered, in such a way that the time-controlled addition of the individually needed detergent components and/or auxiliary agents is made possible.

In a preferred configuration, the apparatuses of the invention include the possibility of the pumping away, and in particular, the circulation, of washing bath liquor through a separate chamber, which is equipped with agents for the, at least partial, separation of the fine-particle solids jointly used in the washing bath, and in particular, the soil-laden trapping agents.

The designing of the vibration elements for the process stage of the ultrasound treatment is based on the data regarding this stage of the new process, indicated in the process part. One or more vibration elements, which are able to give off a prespecified frequency of the ultrasound area or also to give off sliding frequencies, can be present. A continuous and/or pulsating acoustic irradiation of the washing bath with ultrasound is provided by controlling the vibration elements.

In a special configuration, the washing bath has one or more UV radiation sources, whose actuation can be preferably controlled time-staggered in such a way that the treatment of the textile goods in the washing bath is made possible at the desired time in the process.

The apparatuses according to the invention can have devices for an extensive removal of the washing bath from the washed textile in a manner which is in fact known, for which, for example, a time-controlled centrifugation apparatus can be provided. Finally, devices to execute one or more rinse cycles after conclusion of the washing process, in each case with an intermediate stage for the removal of the rinsing liquid, are also provided in a manner which is in fact known.

Example

Washing experiments with various fabric samples provided with standard soils were carried out. The experiments were carried out in a stainless steel vat, which was equipped with ultrasound-producing vibration elements in its bottom.

In particular, the following data were valid for the carrying out of these washing experiments:

1. Capacity of the wash vat: 4 L; ultrasound frequency transmitted to the washing bath: 35 kHz

2. Composition of the washing bath:

0.6 g/L Fatty alcohol sulfate (Sulfopon T55)

1 g/L alpha-$C_{16/18}$ sulfonic-acid disodium salt

0.4 g/L Oleic acid diethanolamide (Comperlan VOD)

0.5 g/L Cosmedia Guar C261 (PQAV)-coated laminated silicate in the sense of P 3,545,990.5 (D 7478/7495); pH 9, adjusted with NaOH

3. Test fabrics used, soiled with standard soil

Cotton, unfinished

Polyester-cotton mixed fabric, finished

Polyester

A mixture of synthetic street dirt and synthetic skin oil was used as soil.

4. Washing conditions in the first process stage to remove pigment and/or grease soils:

Temperature of the washing bath: 41°C

Duration of the acoustic irradiation: 5 min

Continuous acoustic irradiation during the first washing stage.

In the table below, the investigated test fabrics, the pertinent reflectance values of the used soiled material, and the reflectance values of the cleaned material after the ultrasound treatment are summarized.

Table

(1) Gewebe	(2) Ausgangswert (% Remission) (4)	(3) Waschwert (% Remission) (4)	(4) Δ (% Remission)
H-SH-B	27,7	60,6	32,9
H-SH-PBV	30,0	73,8	43,8
H-SH-P	29,5	84,5	55,0

Key: 1 Fabric
2 Starting value
3 Washing value
4 (% Reflectance)

To remove enzyme-specific soils, such as EMPA blood-milk-India ink, on unfinished cotton, 70 mg/L of a protease (Maxatase) were subsequently added to the bath and allowed to act in the manner of a soaking process. To remove bleachable spots (tea, red wine), 0.2-0.5 g/L of a dipercarboxylic acid (diperdodecanedioic acid) were added to the washing bath in a further step. The action of the bleaching agent was supported by the ultrasound mechanics and produced results which corresponded to those attainable in a launderometer.